



# Surface and interfacial tensions of the systems water + *n*-butyl acetate + methanol and water + *n*-pentyl acetate + methanol at 303.15 K

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Received 26 July 2002; accepted 12 November 2002

## Abstract

The surface tension in the homogeneous domain of the ternary liquid mixtures water + *n*-butyl acetate + methanol and water + *n*-pentyl acetate + methanol as well as of the constituent binaries has been measured at 303.15 K and atmospheric pressure. The respective excess surface tension was correlated as a function of the composition using empirical and thermodynamic-based relations. The liquid interfacial tension was measured in the liquid–liquid equilibrium range at the same conditions of temperature and pressure.

A new equation is proposed to correlate the excess surface tension of binary mixtures. This equation can be obtained from the Butler equation and correlates well the excess surface tension data.

The prediction of the surface tension of the binary and ternary systems has been made using the Sprow and Prausnitz model. The Fu et al. and Li et al. models were also applied to predict that property in the ternary systems.

The liquid interfacial tension of the ternary systems was correlated and predicted using the relations proposed by Li and Fu and Fu et al., respectively, with satisfactory results.

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**Keywords:** Surface tension; Interfacial tension; Correlation; Prediction; Water; Methanol; Esters

## 1. Introduction

The surface and liquid interfacial tensions of liquid mixtures are fundamental properties in process design since they play an important role in interphase heat and mass transfer. The experimental data of these properties are required also to test the methods used in prediction and correlation. In particular, for multicomponent systems, the data is scarce which justifies the importance of reliable prediction methods. A few empirical and thermodynamic-based equations are available to correlate the surface tension. Their range of application is usually limited to the binary mixtures, although the thermodynamic-based

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models can correlate the data of multicomponent systems. Among the thermodynamic-based equations, the Butler equation [1] is widely accepted and has been used extensively in different forms. Sonawane and Kumar [2] have developed a model from Butler equation to correlate the surface tension of binary mixtures. Recently, Li et al. [3] proposed a surface tension thermodynamic model for liquid mixtures which is based on the Wilson equation for the excess Gibbs energy. This model correlates very well the experimental data of a large number of binary systems including aqueous systems. Another surface tension correlation was proposed by Fu et al. [4] which is based on the local composition model due to Wilson [5]. Both methods can be applied to the prediction of the surface tension of multicomponent mixtures provided that binary parameters are known.

For the prediction of the surface tension other thermodynamic-based methods are available. Among them, the gradient theory [6] and the Sprow and Prausnitz model [7] are commonly used. The former is generally used for pure substances and binary liquid mixtures. The later is applied to binary and multicomponent mixtures and was selected to be used in this work. The Sprow and Prausnitz model is fully predictive when the activity coefficients of the individual components at the surface and in the bulk liquid are known.

The correlation of liquid interfacial tension in ternary systems with the equilibrium phase compositions is usually made with the method of Fleming et al. [8] and the model due to Li and Fu [9]. The former uses the scaling theory of critical phenomena and the later method is based on a diffuse interface model and is easier to use.

For the prediction of the liquid interfacial tension, several methods are available [10–13]. However, most of them have limited reliable range of application. It will be very important in practical uses if the interfacial tension of multicomponent systems can be predicted only from equilibrium compositions without any adjustable parameters. Fu et al. [4] developed a method which embodies this purpose and is easy to apply.

In this work, we have tested the above referred thermodynamic-based equations to correlate the surface tension data with the composition in the water + methanol, water + ester and ester + methanol systems. A simple equation was developed from the Butler one which has proved to be adequate for highly non-symmetrical binary systems with large values of excess surface tension.

Some empirical methods have been applied. We have chosen the models of Redlich–Kister [14] and Marsh [15] since they are widely used to correlate excess properties.

The methods of Sprow and Prausnitz, Fu et al. and Li et al. were used to predict the ternary surface tension.

The liquid interfacial tension was correlated using the equation of Li and Fu [9]. To predict this property in the water + ester + methanol systems the experimental data found for the binary systems was used in the application of the method proposed by Fu et al. [4].

## 2. Experimental

### 2.1. Materials

Tridistilled water was used. Methanol (Fluka AG) was supplied with a purity >99.8 mass% (HPLC grade). The *n*-butyl acetate (Riedel de H  en) was supplied with a purity >99.7%. For *n*-pentyl acetate (Acros), the reported purity was >99%. The pure component surface tensions measured in this work and the values from literature are gathered in Table 1.

Table 1

Surface tension of the pure components at 303.15 K and interfacial tension of some immiscible binary aqueous mixtures

Component	$\sigma$ (mN m <sup>-1</sup> )	
	Experimental	Literature
Water	71.40	71.40 [16]
<i>n</i> -Butyl acetate	23.60	23.00 [17]
<i>n</i> -Pentyl acetate	24.62	24.68 [16]
Methanol	21.59	21.71 [16]
<i>n</i> -Heptane	19.16	19.17 [16]
Component in the aqueous mixture ( <i>T</i> , K)	$\sigma'$ (mN m <sup>-1</sup> )	
	Experimental	Literature
<i>n</i> -Hexane (293.15)	49.4	49.8 [18]
Benzene (298.15)	33.8	33.8 [13]
<i>n</i> -Heptane (303.15)	49.1	49.3 [13]
Diethylether (298.15)	10.7	11.0 [13]

## 2.2. Measurements

Surface and interfacial tensions were measured using a PC controlled KSV Sigma 70 tension balance which employs the Du Noüy ring-detachment method. The platinum ring was thoroughly cleaned and flamed before each measurement. The measurements were automatically corrected to the actual values by means of the Huh and Mason compensation for interface distortion. To apply this correction, the density was calculated using the experimental data taken from a previous work [19]. For the interfacial tension, the density of each of the two liquid phases was measured in an Anton Paar DMA 60 digital vibrating tube densimeter with a DMA 602 measuring cell with a precision of  $\pm 10^{-5}$  g cm<sup>-3</sup>. Air and tridistilled water were used for the calibration of the densimeter. A Pt resistance thermometer (calibrated against a precision mercury standard, graduate in 0.01 °C, certified by NPL, UK) was placed inside the vibrating tube densimeter. The temperature was maintained at  $303.15 \pm 0.01$  K.

The precision of the surface tension is indicated by the instruction manual of the tension balance to be of the order of  $\pm 0.01$  mN m<sup>-1</sup>. Each experimental point results from a set of about 20 measurements. After the first measurement, there is a tendency to a practically constant value.

The performance of the tension balance was checked by measuring the surface tension of standard pure liquids: tridistilled water and *n*-heptane (LAB-SCAN with a purity >99%). As far as we know, there are not standard mixtures for the calibration of the liquid interfacial tension. Anyway, we have compared our results with those of some immiscible aqueous binary systems. The surface tension data of the binary water + methanol at 303.15 K was also included in the test. The average absolute deviations, %AAD for *M* data points is given by

$$\%AAD = 100 \times \left[ \sum_{i=1}^M \frac{|\sigma_{\text{exp}} - \sigma_{\text{lit}}|}{M} \right] \quad (1)$$

where  $\sigma_{\text{exp}}$  and  $\sigma_{\text{lit}}$  represent the surface tension values of this work and of the literature. These values are 0.3 and 0.4% for water and *n*-heptane, respectively, in the range 20–70 °C. Comparing the experimental

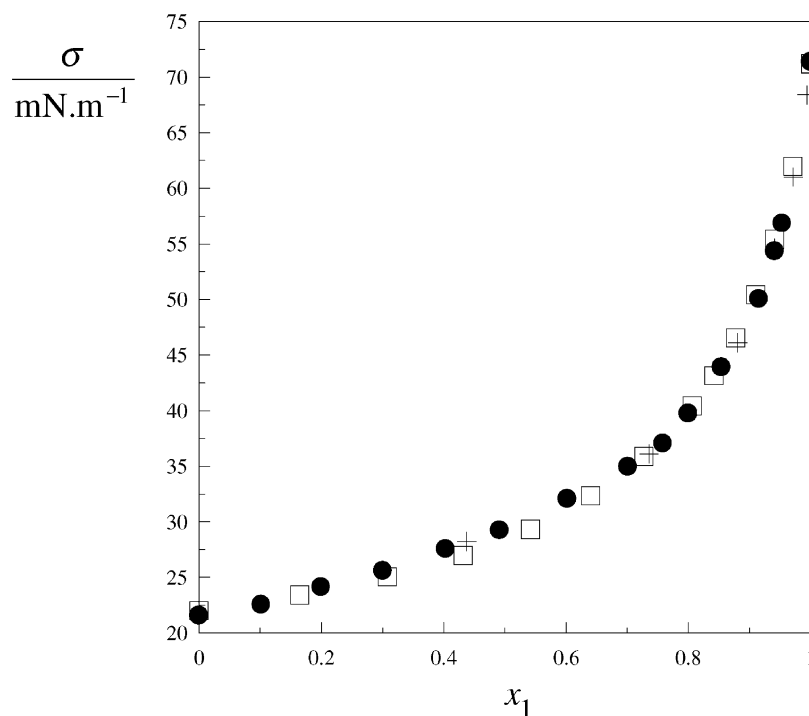


Fig. 1. Surface tension,  $\sigma$ , of the water (1) + methanol (3) system at 303.15 K and atmospheric pressure as a function of the mole fraction: ( $\square$ ) Vázquez et al. [20]; (+) Tamaura et al. [21]; ( $\bullet$ ) this work.

surface tension values of these substances with those from the literature at 303.15 K, one finds the accuracy to be  $\pm 0.01 \text{ mN m}^{-1}$  (see Table 1). A comparison between the measured surface tension and previous published data for water + methanol at 303.15 K is made in Fig. 1. As we can see, the agreement is good. In Table 1, the measured liquid interfacial values of the immiscible aqueous solutions are compared with those given by other authors. The mean absolute deviation is  $0.2 \text{ mN m}^{-1}$ . On the other hand, the value of the accuracy presented in the literature is  $\pm 0.1 \text{ mN m}^{-1}$ , when the same technique is used [9]. Therefore, we have considered that the accuracy is  $\pm 0.1 \text{ mN m}^{-1}$  for our liquid interfacial measurements.

The temperature inside the surface tension measurement vessel was maintained and controlled at  $303.15 \pm 0.10 \text{ K}$  using a Julabo FP50 bath. To measure the surface and the interfacial tension we have planned the distribution of the mixture compositions in the ternary diagram accordingly to the liquid–liquid equilibrium data of Rao and Rao [22]. Mixtures were prepared by mass using a Mettler AT 200 balance with a precision of  $\pm 10^{-5} \text{ g}$ . The precision of the mole fraction is estimated to be of the order  $\pm 10^{-3}$ .

For the liquid interfacial tension measurements, the mixture with a known global composition was kept at 303.15 K in a thermostated vessel and shaken several times during a period of at least 24 h to reach the equilibrium. Samples of the organic and the aqueous phases were withdrawn to measure the density and the liquid interfacial tension. The surface tension of each liquid phase was also measured separately.

### 3. Equations for the surface and the interfacial tension

#### 3.1. Surface tension

The composition dependence of the surface tension of mixtures can be represented in terms of the excess surface tension,  $\sigma^E$ , defined as

$$\sigma^E = \sigma - \sum x_i \sigma_i^* \quad (2)$$

where  $\sigma$  is the surface tension of the mixture, and  $\sigma_i^*$  is the surface tension of the  $i$ th component of mole fraction  $x_i$ .

The excess functions are usually represented by the well known Redlich–Kister (RK) polynomials [14]. For the excess surface tension, it is

$$\sigma^E = x_i x_j \sum_{k=0}^p B_k z_{ij}^k \quad (3)$$

where  $B_k$  are adjustable coefficients and  $z_{ij} = x_i - x_j$ . No more than three coefficients ( $p = 2$ ) were used.

A more flexible equation for representation of the binary excess data is a rational expression proposed by Malanowsky and Marsh (MM) [15]. For the excess surface tension,

$$\sigma^E = x_i x_j \frac{\sum_{k=0}^p B_k z_{ij}^k}{1 + \sum_{l=1}^m C_l z_{ij}^l} \quad (4)$$

where  $B_k$  and  $C_l$  are fitted constants.

A thermodynamic-based equation was proposed by Sonawane and Kumar (SK) [2],

$$\frac{\sigma^E}{RT} = x_i x_j \left( \frac{1}{A_i^*} - \frac{1}{A_j^*} \right) (\delta_p + \delta_m x_j) \quad (5)$$

where the adjustable parameters are  $\delta_p$  and  $\delta_m$ ,  $A_i^*$  and  $A_j^*$  are the molar surface areas of pure components  $i$  and  $j$ , respectively. Eq. (5) is obtained from Butler equation [1]:

$$\sigma = \sigma_i^* + \frac{RT}{A_i^*} \ln \left( \frac{x_{i,s}}{x_i} \right) \quad (i = 1, 2, \dots, N_c) \quad (6)$$

where  $x_{i,s}$  and  $x_i$  denote the mole fractions of the component  $i$  in the surface and bulk phases, respectively and  $N_c$  is the number of components.

Modifying the Hildebrand–Scott equation [23] for ideal binary systems with the local composition model proposed by Wilson [5], Fu et al. (FLW) [4] derived the following equation

$$\sigma = \sum_{i=1}^{N_c} \frac{x_i \sigma_i^*}{\sum_{j=1}^{N_c} x_j f_{ij}} - \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} \frac{x_i x_j |\sigma_i^* - \sigma_j^*|}{\sum_{q=1}^{N_c} x_q f_{iq} \sum_{r=1}^{N_c} x_r f_{jr}} \quad (7)$$

where the  $f_{ij}$  are the binary adjustable parameters. For a binary mixture, the above equation reduces to

$$\sigma = \frac{x_1 \sigma_1^*}{x_1 + x_2 f_{12}} + \frac{x_2 \sigma_2^*}{x_1 f_{21} + x_2} - \frac{x_1 x_2 |\sigma_1^* - \sigma_2^*|}{(x_1 + x_2 f_{12})(x_1 f_{21} + x_2)} \quad (8)$$

From the Wilson equation of the excess Gibbs energy, Li et al. (LWW) [3] derived the equation

$$\sigma^E = -RT \sum_{i=1}^{N_c} \left[ \frac{x_i}{\sum_{j=1}^{N_c} x_j \Lambda_{ij}} \sum_j x_j \left( \frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x} \right] \quad (9)$$

where

$$\Lambda_{ij} = \exp \left( -\frac{U_{ij} - U_{ii}}{RT} \right), \quad \left( \frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x} = -\frac{\Lambda_{ij}}{RT} \left[ \frac{\partial (U_{ij} - U_{ii})}{\partial A} \right]_{T,P,x}$$

In the preceding relations,  $U_{ij} - U_{ii}$  is the difference in the interaction energy between molecular pair  $ij$  and the derivative  $[\partial(U_{ij} - U_{ii})/\partial A]_{T,P,x}$  reflects the energy change with the increase in surface area. In a binary system the adjustable parameters are four, i.e.  $U_{12} - U_{11}$ ,  $U_{21} - U_{22}$ ,  $[\partial(U_{12} - U_{11})/\partial A]_{T,P,x}$  and  $[\partial(U_{21} - U_{22})/\partial A]_{T,P,x}$ . Li et al. [3] made the assumption  $U_{ij} = (U_{ii} + U_{jj})/2$ , reducing the number of parameters to two, i.e.  $U_{12} - U_{11}$  and  $[\partial(U_{12} - U_{11})/\partial A]_{T,P,x}$ . For a binary system, Eq. (9) is written as

$$\sigma^E = -RT \frac{x_1 x_2}{x_1 \Lambda_{21} + x_2} \left( \frac{\partial \Lambda_{21}}{\partial A} \right) \left[ 1 - \frac{1}{\Lambda_{21}} \right] \quad (10)$$

With the parameters in Eqs. (8) and (10) obtained from regression of binary surface tension data, the prediction of this property in multicomponent systems can be obtained.

Sprow and Prausnitz (SP) [7] considered that the bulk and surface phases are in equilibrium and the partial molar surface area of component  $i$ ,  $A_i$ , is the same as the molar surface area of the corresponding pure component,  $A_i^*$ , concluding that

$$\sigma = \sigma_i^* + \frac{RT}{A_i^*} \ln \left( \frac{\gamma_{i,s} x_{i,s}}{\gamma_i x_i} \right) \quad (i = 1, 2, \dots, N_c) \quad (11)$$

where  $\gamma_{i,s}$  and  $\gamma_i$  are the activity coefficients of component  $i$  in the surface and bulk phases, respectively. The  $\gamma_{i,s}$  is related with the surface composition and the  $\gamma_i$  to the bulk liquid composition. The surface tension and the  $N_c$  values of  $x_{i,s}$  are the  $N_c + 1$  unknowns which are calculated with the  $N_c$  (Eq. (11)) and the relation  $\sum x_{i,s} = 1$ . Eq. (11) are used here to predict the surface tension of the binary and the ternary mixtures. We have used the UNIFAC model due to Fredenslund et al. [24] to calculate the activity coefficients  $\gamma_{i,s}$  and  $\gamma_i$ .

All the models referred in this section are summarized in Table 2.

### 3.2. Interfacial tension

To correlate the liquid interfacial tension Li and Fu (LF) [9] proposed the use of the equation

$$\sigma' = \sigma'_0 \left( \frac{X}{X_0} \right)^k \quad (12)$$

where

$$X = -\ln [x_1^\alpha + x_2^\beta + x_{3p}] \quad (13)$$

where  $\sigma'$  is the interfacial tension between the two immiscible liquid phases  $\alpha$  and  $\beta$  in the ternary system and  $\sigma'_0$  is the interfacial tension of the partially miscible binary pair which corresponds  $x_3 = 0$  and

Table 2  
Models for  $\sigma$  and  $\sigma^E$  used in this work

Author	Expression for $\sigma$ (or $\sigma^E$ )	Parameters	Application
This work	$\frac{\sigma^E}{x_i x_j} = A + B(1 - z_{ij})^C$	$A, B$ and $C$	Correlation of binary $\sigma^E$
Sonawane–Kumar (SK)	$\frac{\sigma^E}{RT} = x_i x_j \left( \frac{1}{A_i^*} - \frac{1}{A_j^*} \right) (\delta_p + \delta_m x_j)$	$\delta_p$ and $\delta_m$	Correlation of binary $\sigma^E$
Fu et al. (FLW)	$\sigma = \sum_{i=1}^{N_c} \frac{x_i \sigma_i^*}{\sum_{j=1}^{N_c} x_j f_{ij}} - \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} \frac{x_i x_j  \sigma_i^* - \sigma_j^* }{\sum_{q=1}^{N_c} x_q f_{iq} \sum_{r=1}^{N_c} x_r f_{jr}}$	$f_{ij}, f_{ji}$ for each binary	Correlation of binary and prediction of multicomponent $\sigma$ (or $\sigma^E$ )
Li et al. (LWW)	$\sigma^E = -RT \sum_{i=1}^{N_c} \left[ \frac{x_i}{\sum_j x_j \Lambda_{ij}} \sum_j x_j \left( \frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x} \right]$	$\Lambda_{ij}, \left( \frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x}$	Correlation of binary and prediction of multicomponent $\sigma$ (or $\sigma^E$ )
Sprow–Prausnitz (SP)	$\sigma = \sigma_i^* + \frac{RT}{A_i^*} \ln \left( \frac{\gamma_{i,s} x_{i,s}}{\gamma_i x_i} \right) (i = 1, 2, \dots, N_c)$		Correlation and prediction of multicomponent $\sigma$ (or $\sigma^E$ )
Redlich–Kister (RK)	$\sigma^E = x_i x_j \sum_{k=0}^p B_k z_{ij}^k, z_{ij} = x_i - x_j$	$B_k$	Correlation of binary $\sigma^E$
Malanovsky–Marsh (MM)	$\sigma^E = x_i x_j \frac{\sum_{k=0}^p B_k z_{ij}^k}{1 + \sum_{l=1}^m C_l z_{ij}^l}, z_{ij} = x_i - x_j$	$B_k$ and $C_l$	Correlation of binary $\sigma^E$

$X = X_0$  in Eq. (13);  $x_1^\alpha$  is the mole fraction of component 1 in the liquid phase  $\alpha$  richer in component 2,  $x_2^\beta$  is the mole fraction of component 2 in the phase richer in component 1 and  $x_{3p}$  is the mole fraction of component 3 in the phase poor in it. Li and Fu considered the parameter  $k$  as an adjustable one in Eq. (12) and they used a more general form,  $k = k_1 + k_2 X$  [25].

Fu et al. [4] developed a thermodynamic-based model to predict the liquid interfacial tension of ternary systems from the mutual solubilities. The equation is

$$\sigma' = K \Sigma \quad (14)$$

where

$$\Sigma = \frac{RTX}{A_{w0} \exp(X)(x_1^\alpha q_1 + x_2^\beta q_2 + x_{3r} q_3)} \quad (15)$$

and  $K$  is an adjustable parameter found from binary data. In Eq. (15),

$$X = -\ln[x_1^\alpha + x_2^\beta + x_{3r}] \quad (16)$$

where  $x_1^\alpha$  and  $x_2^\beta$  have the same meaning as before (in Eq. (13)),  $x_{3r}$  is the mole fraction of component 3 in the bulk phase richer in 3,  $T$  is the temperature,  $A_{w0}$  is the van der Waals area of a standard segment ( $A_{w0} = 2.5 \times 10^9 \text{ cm}^2 \text{ mol}^{-1}$  [4]) and  $q_i = A_{wi}/A_{w0}$  is the pure component area parameter of molecule  $i$ . When  $x_3 = 0$ , Eq. (15) takes the form corresponding to binary systems.

## 4. Results and discussion

### 4.1. Surface tension

The measured surface tension and the corresponding excess surface tension as a function of the composition for the ternary systems water + *n*-butyl acetate + methanol and water + *n*-pentyl acetate + methanol at 303.15 K and atmospheric pressure are shown in Tables 3 and 4, respectively. Results for the constituent binaries water + methanol, ester + methanol and water + ester are also included. To correlate the excess functions,  $X^E$ , with the mole fraction in binary systems, analytical models in which the dependent variable is  $X^E/x_i x_j$ , is often used (e.g. Redlich–Kister model). In Fig. 2, the quantity  $\sigma^E/x_i x_j$  is represented as a function of  $z_{ij}$  for the binary systems water + methanol and ester + methanol. A simple new equation to describe the observed behavior is of the form

$$\frac{\sigma^E}{x_i x_j} = A + B(1 - z_{ij})^C \quad (17)$$

where  $A$ ,  $B$  and  $C$  are adjustable parameters. In Fig. 2, the curves obtained from Eq. (17) are also plotted. As can be seen from Fig. 2, the new equation correlates well the surface tensions of these systems even for the system water + methanol which is highly non-symmetrical with large values of  $\sigma^E$ . Eq. (17) can be obtained from Butler equation (Eq. (6)) (see Appendix A).

The excess surface tension for the ternary mixtures,  $\sigma_{123}^E$ , have been fitted to the equation

$$\sigma_{123}^E = \sigma_{12}^E + \sigma_{13}^E + \sigma_{23}^E + \sigma_T^E \quad (18)$$



Table 3

Experimental surface tension,  $\sigma$ , and excess surface tension,  $\sigma^E$ , for the system water (1) + *n*-butyl acetate (2) + methanol (3) at 303.15 K and atmospheric pressure

$x_1$	$x_2$	$\sigma$ (mN m <sup>-1</sup> )	$\sigma^E$ (mN m <sup>-1</sup> )	$x_1$	$x_2$	$\sigma$ (mN m <sup>-1</sup> )	$\sigma^E$ (mN m <sup>-1</sup> )
0.044	0.498	23.34	-1.44	0.451	0.049	25.89	-18.26
0.051	0.757	23.64	-2.01	0.498	0.039	26.31	-20.16
0.054	0.736	23.63	-2.13	0.507	0.079	24.86	-22.14
0.054	0.250	22.96	-1.82	0.551	0.049	25.50	-23.63
0.055	0.444	23.27	-1.95	0.587	0.020	27.35	-23.52
0.055	0.845	23.77	-2.26	0.014	0.986	23.73	-0.54
0.055	0.637	23.65	-1.96	0.020	0.980	23.76	-0.80
0.056	0.548	23.43	-2.05	0.027	0.973	23.78	-1.11
0.059	0.831	23.79	-2.41	0.032	0.968	23.83	-1.30
0.060	0.050	22.67	-2.01	0.038	0.962	23.91	-1.51
0.061	0.452	23.31	-2.23	0.041	0.959	23.94	-1.62
0.096	0.397	23.47	-3.70	0.046	0.954	23.95	-1.85
0.099	0.300	23.47	-3.65	0.052	0.948	24.03	-2.06
0.102	0.578	23.12	-4.71	0.101	0	22.57	-4.05
0.103	0.686	23.86	-4.24	0.199	0	24.16	-7.34
0.112	0.746	23.94	-4.73	0.300	0	25.61	-10.92
0.131	0.618	23.97	-5.39	0.403	0	27.60	-14.06
0.153	0.049	23.62	-5.69	0.491	0	29.28	-16.77
0.153	0.443	23.79	-6.31	0.602	0	32.08	-19.50
0.154	0.393	23.66	-6.39	0.701	0	34.98	-21.53
0.156	0.148	23.53	-6.13	0.758	0	37.06	-22.29
0.172	0.498	23.92	-7.24	0.800	0	39.76	-21.68
0.175	0.550	23.93	-7.48	0.854	0	43.91	-20.22
0.192	0.302	23.85	-7.91	0.915	0	50.09	-17.08
0.193	0.197	23.79	-7.81	0.941	0	54.35	-14.11
0.199	0.486	24.16	-8.32	0.953	0	36.80	-12.18
0.209	0.359	23.73	-8.99	0	0.082	21.88	0.13
0.225	0.445	23.70	-9.99	0	0.104	22.04	0.24
0.241	0.051	24.44	-9.26	0	0.155	22.21	0.31
0.273	0.353	24.15	-11.75	0	0.188	22.31	0.34
0.284	0.020	25.10	-10.68	0	0.242	22.44	0.36
0.297	0.101	24.87	-11.72	0	0.353	22.70	0.40
0.300	0.196	24.33	-12.60	0	0.394	22.81	0.43
0.309	0.292	23.93	-13.64	0	0.510	23.06	0.44
0.333	0.203	24.44	-14.14	0	0.662	23.37	0.45
0.334	0.240	24.46	-14.25	0	0.669	23.43	0.44
0.344	0.153	24.51	-14.52	0	0.748	23.46	0.37
0.395	0.101	25.07	-16.40	0	0.799	23.51	0.31
0.399	0.046	25.80	-15.76	0	0.927	23.55	0.10
0.402	0.178	24.58	-17.39	0	0.960	23.58	0.06
0.442	0.043	26.12	-17.57				
0.449	0.101	24.83	-19.33				
0.449	0.140	24.53	-19.71				

Table 4

Experimental surface tension,  $\sigma$ , and excess surface tension,  $\sigma^E$ , for the system water (1) + *n*-pentyl acetate (2) + methanol (3) at 303.15 K and atmospheric pressure

$x_1$	$x_2$	$\sigma$ (mN m <sup>-1</sup> )	$\sigma^E$ (mN m <sup>-1</sup> )	$x_1$	$x_2$	$\sigma$ (mN m <sup>-1</sup> )	$\sigma^E$ (mN m <sup>-1</sup> )
0.031	0.021	22.08	-1.12	0.403	0.100	25.72	-16.25
0.042	0.121	22.66	-1.39	0.435	0.100	25.23	-18.33
0.062	0.498	23.12	-3.07	0.461	0.040	26.78	-17.89
0.065	0.339	22.88	-2.97	0.504	0.040	26.72	-20.10
0.065	0.586	23.38	-3.22	0.546	0.020	27.98	-20.87
0.084	0.059	22.88	-3.07	0.016	0.984	24.65	-0.72
0.101	0.399	24.10	-3.73	0.033	0.967	24.69	-1.47
0.103	0.296	23.72	-3.90	0.047	0.953	24.72	-2.10
0.124	0.041	23.31	-4.58	0.069	0.931	24.77	-3.08
0.127	0.119	23.54	-4.74	0.089	0.911	24.82	-3.96
0.144	0.422	23.48	-6.56	0.096	0.904	24.84	-4.27
0.165	0.163	23.97	-6.33	0	0.900	24.08	-0.24
0.179	0.445	23.78	-8.07	0	0.799	23.65	-0.36
0.200	0.206	24.07	-8.11	0	0.693	23.31	-0.38
0.203	0.042	24.15	-7.68	0	0.602	23.03	-0.38
0.204	0.345	23.82	-8.98	0	0.500	22.74	-0.37
0.266	0.288	24.59	-11.12	0	0.407	22.52	-0.30
0.298	0.207	24.67	-12.39	0	0.352	22.34	-0.32
0.309	0.100	24.68	-12.60	0	0.280	22.21	-0.23
0.362	0.041	25.59	-14.16	0	0.197	22.02	-0.17
0.377	0.161	24.91	-15.95	0	0.103	21.81	-0.09

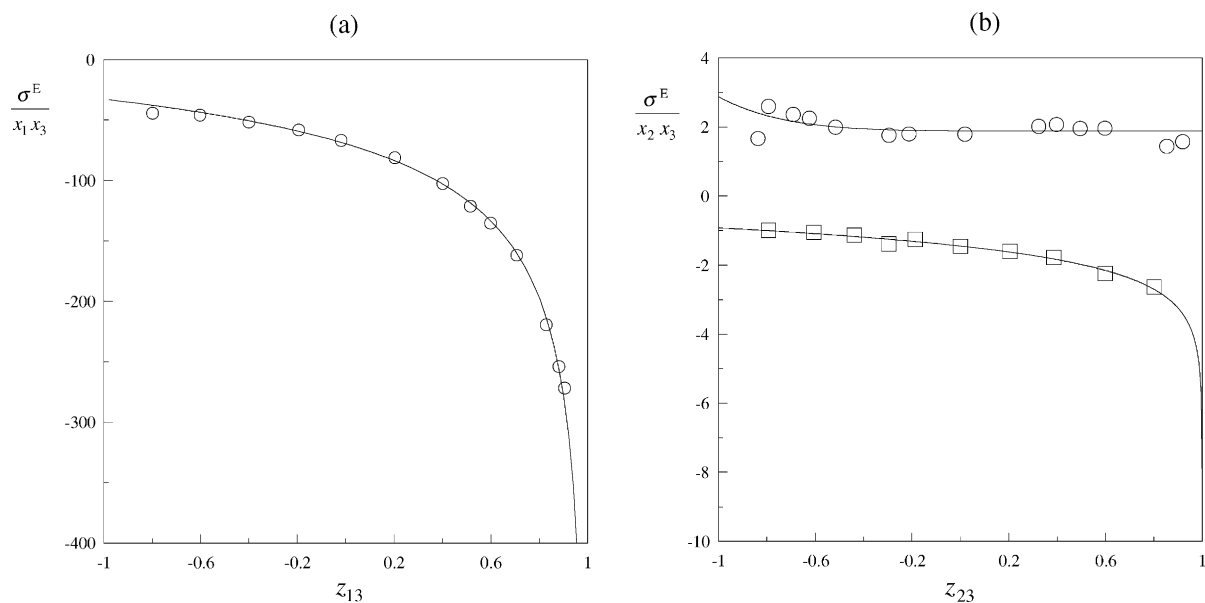


Fig. 2.  $\sigma^E/x_i x_j$  as function of  $z_{ij} (= x_i - x_j)$ . The symbols correspond to our experimental measurements and the curves represent Eq. (17): (a) water (1) + methanol (3); (b) ester (2) + methanol (3): (○) *n*-butyl acetate + methanol; (□) *n*-pentyl acetate + methanol.

Table 5

Coefficients of Eqs. (17) and (19) fitted to the excess surface tension,  $\sigma^E$  (mN m<sup>-1</sup>), for the binary and ternary systems

System	A	B	C	S (mN m <sup>-1</sup> )	
Water + methanol	108.530	-178.258	-0.335	0.45	
Water + <i>n</i> -butyl acetate	-41.606	0	0	0.02	
<i>n</i> -Butyl acetate + methanol	1.879	0.005	7.598	0.03	
Water + <i>n</i> -pentyl acetate	-48.458	0	0	0.06	
<i>n</i> -Pentyl acetate + methanol	38.907	-40.357	-0.019	0.02	
	$D_1$	$D_2$	$D_3$	$D_4$	S (mN m <sup>-1</sup> )
Water + <i>n</i> -butyl acetate + methanol	-60.213	-141.978	-95.357	-1.553	0.18
Water + <i>n</i> -pentyl acetate + methanol	-23.998	-156.136	-66.983	-1.567	0.26

The standard deviation of the fitting,  $S$ , is defined by Eq. (20).where the ternary term,  $\sigma_T^E$ , is given by

$$\sigma_T^E = x_1 x_2 x_3 \frac{D_1 + D_2(x_1 - x_2) + D_3(x_2 - x_3)}{1 + D_4(x_1 - x_2)} \quad (19)$$

and  $\sigma_{ij}^E$  represents the excess surface tension for the binaries which is given by Eq. (17). Eq. (19) is similar to the one proposed by Pando et al. [26] for representation of ternary  $V^E$  data and have also the form of Eq. (4). For the water + ester binary, only one parameter was considered in  $\sigma_{12}^E$  since the components are practically immiscible. The coefficients  $A$ ,  $B$ ,  $C$  (Eq. (17)),  $D_i$  (Eq. (19)) and the standard deviations,  $S$ , obtained from the Levenberg–Marquardt method of fitting, are given in Table 5. The standard deviation of the fitting is defined as

$$S = \left[ \sum_{i=1}^M \frac{(\sigma_{\text{exp}}^E - \sigma_{\text{calc}}^E)_i^2}{M - N} \right]^{1/2} \quad (20)$$

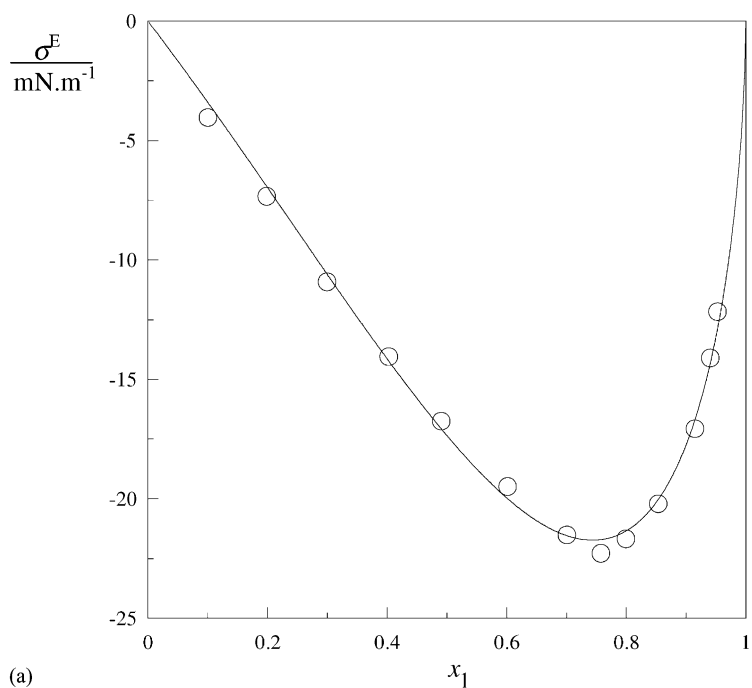
where  $\sigma_{\text{exp}}^E$  and  $\sigma_{\text{calc}}^E$  are the experimental and calculated excess surface tension and  $N$  is the number of adjustable parameters. As we can see, the fittings of binary and ternary data are good.

The experimental values and the fitted curves  $\sigma^E$  for the binaries water + methanol and ester + methanol as a function of the composition are plotted in Fig. 3. A three-dimensional surface of  $\sigma$  calculated from Eq. (18) for the system water + *n*-butyl acetate + methanol is plotted in Fig. 4. For the system water + *n*-pentyl acetate + methanol, a similar plot is obtained. Small values of  $\sigma$  are observed in a wide range of composition, practically in the whole homogeneous region.

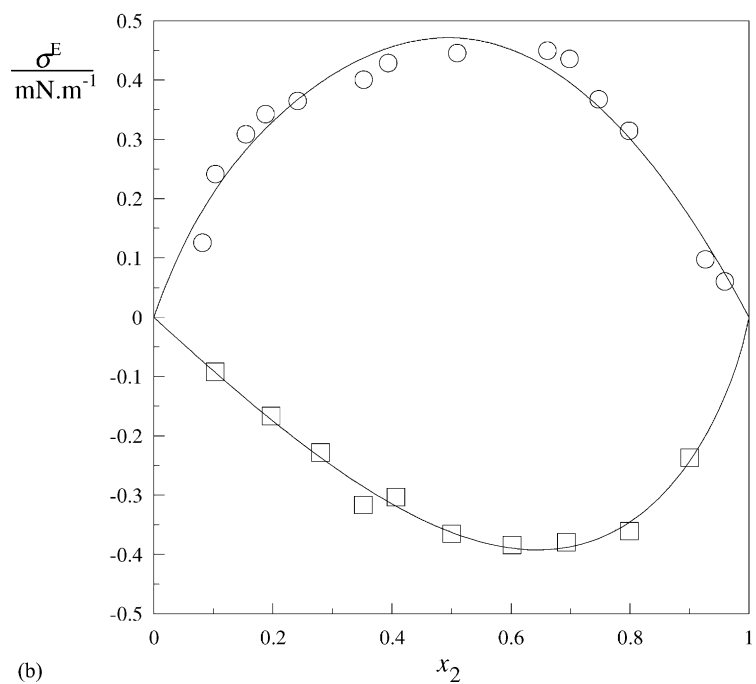
The equations given in Section 3 were applied to the correlation of the surface tension of the binary systems. For the application of the Sonawane and Kumar model, the molar surface areas,  $A_i^*$ , of pure components needed as input data in Eq. (5) were calculated from the correlation proposed by Suarez et al. [27]:

$$A_i = 1.021 \times 10^8 V_c^{6/15} V_b^{4/15} \quad (21)$$

where  $V_c$  is the critical molar volume and  $V_b$  is the bulk liquid molar volume. The values of  $V_c$  were taken from Sato et al. [28], Goodwin [29], Steele et al. [30] and Poling et al. [31] for water, methanol,



(a)



(b)

Fig. 3. Excess surface tension,  $\sigma^E$ , as a function of the composition. The symbols correspond to the experimental data and the curves represent Eq. (17): (a) water (1) + methanol (3); (b) ester (2) + methanol (3): (○) *n*-butyl acetate + methanol; (□) *n*-pentyl acetate + methanol.

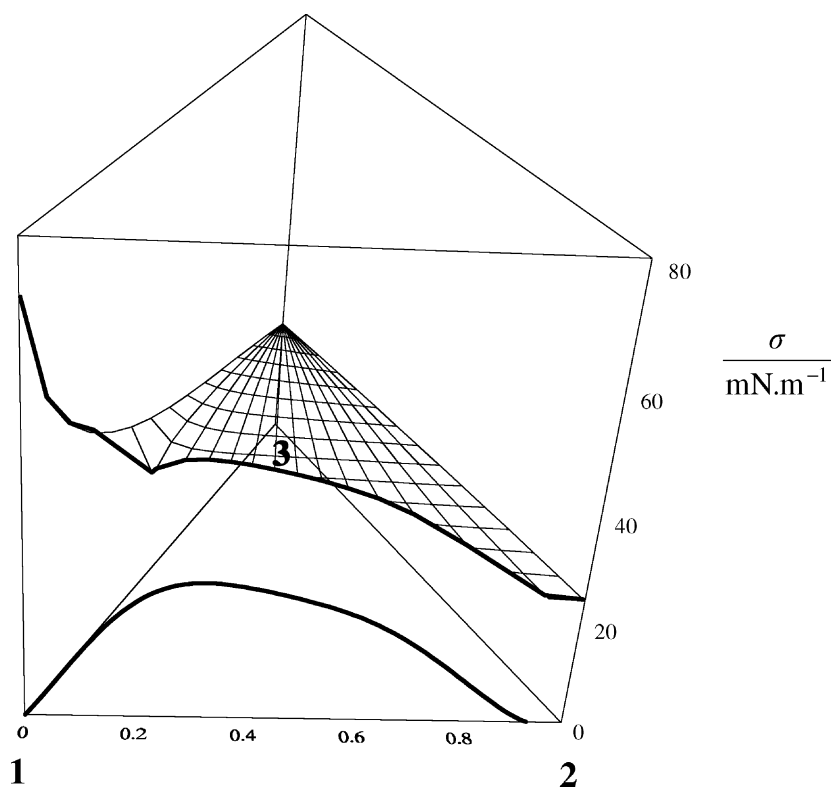


Fig. 4. Three-dimensional representation of  $\sigma$  ( $\text{mN m}^{-1}$ ) for water + *n*-butyl acetate + methanol at 303.5 K and atmospheric pressure, calculated using parameters of Eq. (18).

*n*-butyl acetate and *n*-pentyl acetate, respectively. The molar volume at 303.15 K were calculated from the density given in a previous work [19].

In Table 6, the adjusted coefficients of the equations used to correlate the binary data are listed as well as the respective standard deviations of the fittings. The average absolute deviation of the surface tension is also indicated. As expected the highest values of the standard deviation are obtained for the water + methanol system which have higher values of  $\sigma^E$  and shows a markedly asymmetrical variation of this property with the composition. With the exception of the SK model all the thermodynamic-based equations correlate well the surface tension. The AAD is of the same order of magnitude in all the models. The SK model does not give good results since it embodies a linear dependence of  $\sigma^E/x_1x_3$  in the composition.

It is interesting to note that the parameters  $U_{12} - U_{11}$  and  $[\partial(U_{12} - U_{11})/\partial A]_{T,P,x}$  of the Li et al. model are negative for all the binary systems. For the system, water + methanol are similar to the ones reported in [3].

Which concerns to the use of the empirical models (RK-3 and MM-2), we observe that the MM-2 equation has a similar performance as the thermodynamic models with the same number of adjustable parameters. The RK-3 equation give similar results to the other equations when  $\sigma^E$  is low.

Table 6

Coefficients, standard deviation,  $S$ , and absolute average deviation, %AAD of the models used to correlate surface tension with the composition for the binary systems

System (1 + 2)	Model	$A$	$B$	$C$	$S$ (mN m <sup>-1</sup> )	%AAD
Water + methanol	This work	108.530	-178.258	-0.335	0.45	1.1
	BSK <sup>a</sup>	-18.117	19.055	-	3.58	8.0
	LWW <sup>b</sup>	0.0947	$-1.554 \times 10^{-6}$	-	0.21	0.5
	LWW <sup>c</sup>	-714.54	-497.46	-	0.21	0.5
	FLW <sup>d</sup>	1.726	0.0818	-	0.27	0.6
	RK-3 <sup>e</sup>	-63.844	-76.899	-94.277	1.82	3.9
	MM-2 <sup>f</sup>	-68.395	-0.827	-	0.21	0.5
Water + <i>n</i> -butyl acetate	This work	-41.606	0	0	0.02	0.1
	LWW <sup>b</sup>	0.447	$-1.303 \times 10^{-5}$	-	0.02	0.1
	LWW <sup>c</sup>	-244.10	-883.68	-	0.02	0.1
	FLW <sup>d</sup>	1.214	0.521	-	0.02	0.1
<i>n</i> -Butyl acetate + methanol	This work	1.879	0.005	7.598	0.03	0.1
	BSK <sup>a</sup>	-0.2436	-0.0258	-	0.04	0.1
	LWW <sup>b</sup>	1.1167	$-7.761 \times 10^{-6}$	-	0.04	0.1
	LWW <sup>c</sup>	33.47	-210.68	-	0.04	0.1
	FLW <sup>d</sup>	0.8693	0.9625	-	0.04	0.1
	RK-3 <sup>e</sup>	1.8345	-0.0596	0.5426	0.03	0.1
	MM-2 <sup>f</sup>	1.932	0.0551	-	0.04	0.1
Water + <i>n</i> -pentyl acetate	This work	-48.458	0	0	0.06	0.2
	LWW <sup>b</sup>	0.0668	$-1.272 \times 10^{-6}$	-	0.00	0.0
	LWW <sup>c</sup>	-820.34	-577.26	-	0.00	0.0
	FLW <sup>d</sup>	2.923	0.270	-	0.00	0.0
<i>n</i> -Pentyl acetate + methanol	This work	38.907	-40.357	-0.019	0.02	0.0
	BSK <sup>a</sup>	0.2997	-0.2204	-	0.03	0.1
	LWW <sup>b</sup>	0.28307	$-1.456 \times 10^{-7}$	-	0.01	0.0
	LWW <sup>c</sup>	-382.59	-15.59	-	0.01	0.0
	FLW <sup>d</sup>	1.393	0.634	-	0.05	0.2
	RK-3 <sup>e</sup>	-1.443	-0.886	-0.562	0.02	0.1
	MM-2 <sup>f</sup>	-1.4487	-0.5588	-	0.01	0.0

<sup>a</sup> The coefficients  $A$  and  $B$  correspond to  $\delta_p$  and  $\delta_m$ , respectively.

<sup>b</sup> The coefficients  $A$  and  $B$  correspond to  $A_{21}$  and  $(\partial A_{21}/\partial A)_{T,P,x}$ , respectively.

<sup>c</sup> The values given correspond to  $U_{12} - U_{11}/R$  (in K) and  $10^5 \times [\partial(U_{12} - U_{11})/\partial A]_{P,T,x}/R$  (in K mol<sup>-1</sup> m<sup>-2</sup>), respectively.

<sup>d</sup> The coefficients correspond to  $f_{12}$  and  $f_{21}$ , respectively.

<sup>e</sup> The coefficients  $A$ ,  $B$  and  $C$  correspond to  $B_0$ ,  $B_1$  and  $B_2$ , respectively.

<sup>f</sup> The coefficients  $A$  and  $B$  correspond to  $B_0$  and  $C_0$ , respectively.

The surface tension of the ternary systems was predicted using the methods of Li et al. [3] and Fu et al. [4]. The binary coefficients needed to the calculations are listed in Table 6. The predictive method of Sprow and Prausnitz was applied to the binary and ternary systems. The results of the predictions with the equations above mentioned are given in Table 7. With the exception of the water + methanol system the fully predictive method of Sprow and Prausnitz allows good results as seen by the low AAD values. Suarez et al. [27] using the same method and a modified UNIFAC model obtained AAD values

Table 7

Average absolute deviation, %AAD obtained for the models used to predict surface tension

System	Model	%AAD
Water + methanol	SP	6.0
<i>n</i> -Butyl acetate + methanol	SP	0.5
<i>n</i> -Pentyl acetate + methanol	SP	2.4
Water + <i>n</i> -butyl acetate + methanol	SP	1.3
	LWW	11.5
	FLW	5.2
Water + <i>n</i> -pentyl acetate + methanol	SP	2.1
	LWW	2.9
	FLW	2.8

of 3% for a set of aqueous binary systems and 4% for aqueous ternary systems. For the model (LWW), the difference in AAD for the ternary systems is probably due to the smaller immiscibility range for the system water + *n*-butyl acetate which makes difficult the determination of the model parameters for this binary (see Tables 3 and 4). As far as we know, the FLW and LWW models had been only applied to ternary systems with complete miscibility [3,4]. It is important to stress that these models can also give good predictions for systems with a large immiscibility range.

Table 8

Experimental liquid interfacial tension,  $\sigma'$ , for the ternary systems water (1) + *n*-butyl acetate (2) + methanol (3) and water (1) + *n*-pentyl acetate (2) + methanol (3) at 303.15 K and atmospheric pressure

Overall composition		Water layer			Organic layer			$\sigma'$ (mN m <sup>-1</sup> )
$x_1$	$x_3$	$x_1$	$x_3$	$\sigma$ (mN m <sup>-1</sup> )	$x_1$	$x_3$	$\sigma$ (mN m <sup>-1</sup> )	
Water (1) + <i>n</i> -butyl acetate (2) + methanol (3)								
0.918	0	0.999	0	—	0.067	0	—	13.4
0.546	0.033	0.967	0.033	61.50	0.080	0.033	24.15	12.1
0.797	0.051	0.950	0.049	52.36	0.076	0.049	24.10	10.1
0.786	0.080	0.901	0.098	49.24	0.091	0.099	24.08	9.0
0.495	0.109	0.895	0.105	48.61	0.110	0.110	24.01	7.0
0.630	0.174	0.830	0.167	35.00	0.130	0.185	24.00	5.5
0.745	0.177	0.820	0.175	33.56	0.149	0.201	23.92	4.7
0.600	0.200	0.800	0.195	31.89	0.140	0.215	23.89	4.7
0.620	0.236	0.734	0.258	26.06	0.175	0.275	23.17	3.7
0.599	0.255	0.740	0.250	29.41	0.180	0.270	23.76	2.5
Water (1) + <i>n</i> -pentyl acetate (2) + methanol (3)								
0.848	0	0.999	0	—	0.111	0	—	15.2
0.765	0.020	0.980	0.020	40.98	0.111	0.020	24.06	11.6
0.849	0.051	0.946	0.054	30.40	0.115	0.050	23.89	10.1
0.814	0.085	0.914	0.085	26.56	0.118	0.080	26.56	9.3
0.720	0.180	0.816	0.184	25.94	0.130	0.170	23.23	6.2

The surface tension,  $\sigma$ , and the compositions of the liquid phases at equilibrium are also listed.

Table 9

Coefficients of Eq. (12) fitted to the liquid interfacial tension,  $\sigma'$  (mN m<sup>-1</sup>), for the ternary systems

$X_0$	$\sigma'_0$ (mN m <sup>-1</sup> )	$k$		$S$ (mN m <sup>-1</sup> )
		$k_1$	$k_2$	
Water (1) + <i>n</i> -butyl acetate (2) + methanol (3)				
2.688	13.4	1.067	0	0.7
		1.431	−0.278	0.6
Water (1) + <i>n</i> -pentyl acetate (2) + methanol (3)				
2.192	15.2	1.724	0	1.2
		0.049	1.145	1.0

#### 4.2. Interfacial tension

The experimental liquid interfacial tension and the values of the surface tension of the aqueous and organic phases of the systems water + ester + methanol are listed in Table 8.

The interfacial tension was fitted with Eq. (12) using the interfacial tension of the binary water + ester,  $\sigma'_0$ , as an input value. The parameter  $k$  as been calculated considering that  $k = k_1$  and that  $k = k_1 + k_2X$ . The results of the fittings are listed in Table 9 and in Fig. 5, we represent the liquid interfacial tension,  $\sigma'$  as a function of  $X$ . From this figure, we see that the liquid interfacial tension of the system water + *n*-butyl acetate + methanol is represented adequately by any of the models while for the water + *n*-pentyl acetate

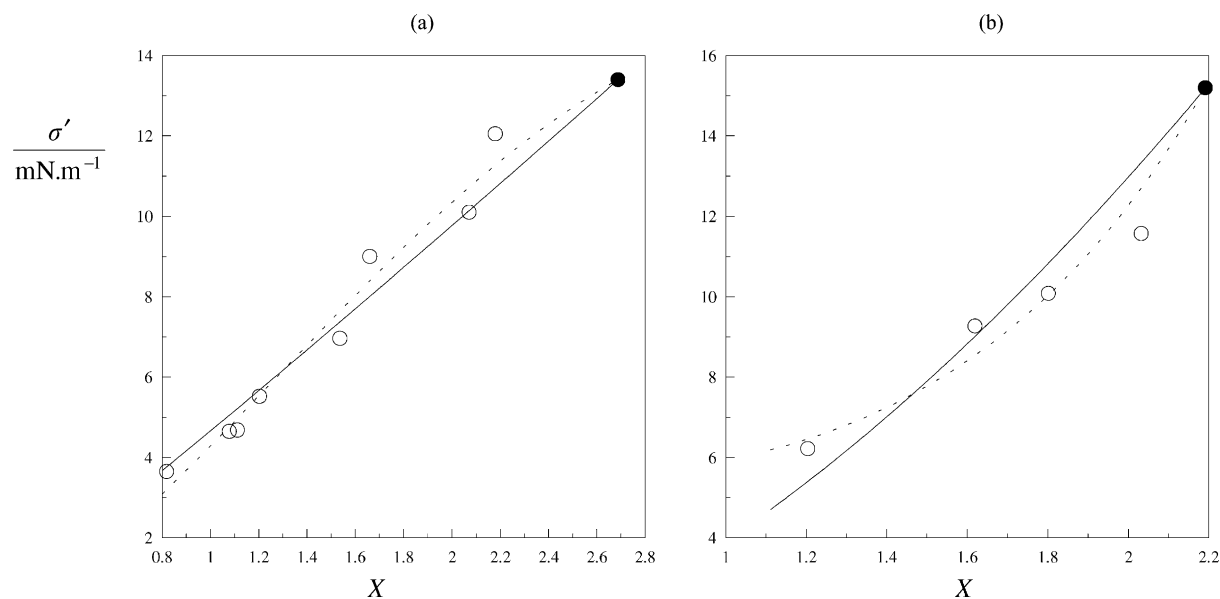


Fig. 5. Liquid interfacial tension,  $\sigma'$ , as a function of  $X$  for the ternary systems water + *n*-butyl acetate + methanol (a) and water + *n*-pentyl acetate + methanol (b). The symbols (●) and (○) represent the experimental data of the binary and ternary systems, respectively, and the lines the curves fitted with the Li et al. model (Eq. (12)): (—)  $k = \text{constant}$  and (---)  $k = k_1 + k_2X$ .



+ methanol a more accurate representation of  $\sigma'$  is possible taking into account the dependence of  $k$  on the composition.

For the calculations with Eq. (14), we have used the binary liquid interfacial tension data,  $\sigma'_0$  reported by Fu et al. [4] for which  $\sigma'_0$  is less than  $20 \text{ mN m}^{-1}$  since higher values show a different dependence in the parameter  $\Sigma$ . It is important to note that our ternary data have values in the range  $2\text{--}16 \text{ mN m}^{-1}$ . From the above referred data, we obtained that

$$\sigma'_0 = (0.717 \pm 0.034) \Sigma \quad (22)$$

Using only the values of  $\sigma'_0$  for the binary systems of the type water + ester the result is

$$\sigma'_0 = (0.806 \pm 0.081) \Sigma \quad (23)$$

The liquid interfacial tension data of the binary and ternary systems as a function of the parameter  $\Sigma$  is represented in Fig. 6. The predictions with Eqs. (22) and (23) are plotted in the same figure. These equations can predict the ternary liquid interfacial tension quite well since the deviation between the experimental data and the calculated values from Eqs. (22) and (23) are low in most of the cases. The AAD is about 8% for the two ternary systems when Eq. (22) is applied. For the system water + *n*-pentyl acetate + methanol the AAD is only 3% using Eq. (23). It is important to stress that the prediction of the ternary liquid interfacial tension was made using only the data from the binary systems.

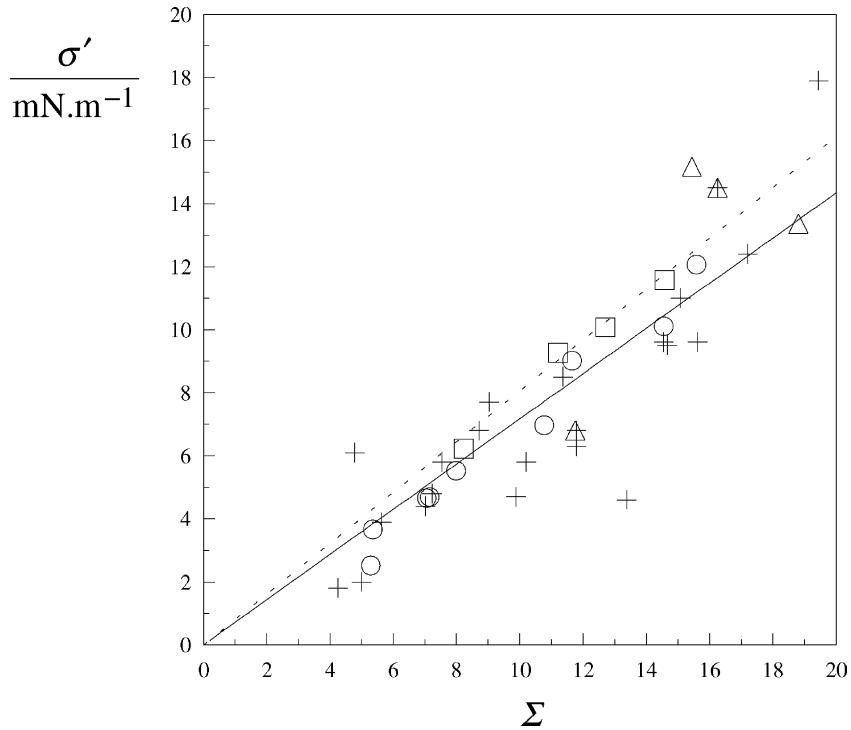


Fig. 6. Liquid interfacial tension,  $\sigma'$ , as a function of  $\Sigma$ : (+) data of binary systems given by Fu et al. [4] including some systems ( $\Delta$ ) water + ester; (—) Eq. (14) with  $K = 0.717$ ; (---) Eq. (14) with  $K = 0.806$ . Our ternary data: ( $\circ$ ) water + *n*-butyl acetate + methanol; ( $\square$ ) water + *n*-pentyl acetate + methanol.

## 5. Conclusions

For the system water + *n*-butyl acetate + methanol at 303.15 K, the excess surface tension is negative in the whole composition range except for the *n*-butyl acetate + methanol system. For the water + *n*-pentyl acetate + methanol mixtures all the values are negative. The surface tension in the ternary homogeneous region of both systems lie in the range 21–27 mN m<sup>-1</sup>.

For the binary systems with low surface tension, the performance of correlations either thermodynamic or empirical is similar. Since the water + methanol system presents an highly asymmetrical behavior of  $\sigma^E$  versus composition, all the models give slightly worse results as can be seen by the higher standard deviation and the average absolute deviation values reported in Table 6.

The equation proposed in this work, Eq. (17), based in the Butler expression correlates the data as well as the other models. One of the advantages of the new model is the analytical simplicity and the possibility of correlation of the surface and bulk compositions, using the fitted parameters (see Appendix A).

The ternary data was also well correlated using pair additivity and a ternary term which is a rational function of the composition leading to standard deviations of about 0.2 mN m<sup>-1</sup>.

Which concerns the prediction of the surface tension all the methods give satisfactory results in spite of the large immiscibility gap exhibited by the ternaries. With few exceptions, the AAD values are less than 3% for the systems studied.

The simple equation of Li and Fu correlates well the liquid ternary interfacial tension data. The standard deviation of the fittings is usually less than 1 mN m<sup>-1</sup>. The prediction of this property with Li et al. method is good, using only binary data for water + ester systems.

### List of symbols

$A$	adjustable parameter of Eq. (17)
$A_i^*$	molar surface area of pure component $i$
AAD	average absolute deviation
$B$	adjustable parameter of Eq. (17)
$B_k$	adjustable parameter of Eqs. (3) and (4)
$C$	adjustable parameter of Eq. (17)
$C_l$	adjustable parameter of Eq. (4)
$f_{ij}$	adjustable parameter of Eq. (7)
$M$	number of experimental points
$N$	number of parameters of Eq. (20)
$N_c$	number of components
$q_i$	area parameter of molecule $i$
$R$	universal gas constant
$S$	standard deviation
$T$	temperature
$U$	interaction energy
$V$	molar volume
$x_i$	liquid mole fraction of the $i$ th component
$X$	defined by Eqs. (13) and (16)

*Greek letters*

$\gamma$	activity coefficient
$\delta_p, \delta_m$	adjustable parameters of Eq. (5)
$\Lambda_{ij}$	Wilson binary parameter
$\sigma$	surface tension
$\sigma'$	liquid interfacial tension
$\Sigma$	defined by Eq. (15)

*Superscripts*

E	excess property
*	pure component

*Subscripts*

b	bulk phase
c	critical point
calc	calculated value
exp	experimental value
$i, j$	components
s	surface phase
T	ternary

**Appendix A**

The Butler equation correlates the surface tension of a binary mixture,  $\sigma$ , with that of pure components,  $\sigma_1^*$  and  $\sigma_2^*$  as

$$\sigma = \sigma_1^* + \frac{RT}{A_1^*} \ln \left( \frac{x_{1,s}}{x_1} \right) \quad (\text{A.1})$$

and

$$\sigma = \sigma_2^* + \frac{RT}{A_2^*} \ln \left( \frac{x_{2,s}}{x_2} \right) \quad (\text{A.2})$$

where  $A_1^*$  are the molar surface area of pure component 1 and  $x_{1,s}$  and  $x_1$  denote the mole fractions of the component 1 in the surface and bulk phases, respectively with similar definitions for component 2.

Multiplication of Eqs. (A.1) and (A.2) by  $x_1$  and  $x_2$ , respectively and adding them results

$$\sigma^E = RT \left[ \frac{x_1}{A_1^*} \ln \left( \frac{x_{1,s}}{x_1} \right) + \frac{x_2}{A_2^*} \ln \left( \frac{x_{2,s}}{x_2} \right) \right] \quad (\text{A.3})$$

where  $\sigma^E$  is the excess surface tension. In order to obtain  $\sigma^E$  from Eq. (A.3), some relationships between  $x_{1,s}$  and  $x_1$  and between  $x_{2,s}$  and  $x_2$  are required. Considering like Sonawane and Kumar did [2], the dimensionless parameters  $\delta_p$  and  $\delta_m$  and that

$$x_{1,s} = x_1 + x_1 x_2 \delta_p + x_1 x_2^{\sigma'} \delta_m \quad (\text{A.4})$$

bearing in mind that  $x_{1,s} + x_{2,s} = 1$ , we obtain

$$x_{2,s} = x_2 - x_1 x_2 \delta_p - x_1 x_2^{c'-1} \delta_m \quad (\text{A.5})$$

When  $c' = 2$ , this definition of surface mole fractions is the same as the one proposed by Sonawane and Kumar [2]. From Eqs. (A.4) and (A.5), the ratios of the mole fractions in the surface and bulk phases can be obtained:

$$\ln \left( \frac{x_{1,s}}{x_1} \right) = \ln (1 + x_2 \delta_p + x_2^{c'-1} \delta_m) \quad (\text{A.6})$$

and

$$\ln \left( \frac{x_{2,s}}{x_2} \right) = \ln (1 - x_1 \delta_p - x_1 x_2^{c'-1} \delta_m) \quad (\text{A.7})$$

These equations can be written as

$$\ln \left( \frac{x_{1,s}}{x_1} \right) = \ln [1 + x_2 (\delta_p + x_2^{c'-1} \delta_m)] \quad (\text{A.8})$$

and

$$\ln \left( \frac{x_{2,s}}{x_2} \right) = \ln [1 - x_1 (\delta_p + x_2^{c'-1} \delta_m)] \quad (\text{A.9})$$

Defining  $\delta = \delta_p + x_2^{c'-1} \delta_m$ , and after substitution of this expression in Eqs. (A.8) and (A.9) results

$$\ln \left( \frac{x_{1,s}}{x_1} \right) = \ln (1 + x_2 \delta) \quad (\text{A.10})$$

and

$$\ln \left( \frac{x_{2,s}}{x_2} \right) = \ln (1 - x_1 \delta) \quad (\text{A.11})$$

Substitution of Eqs. (A.10) and (A.11) in Eq. (A.3) yields to

$$\sigma^E = RT \left[ \frac{x_1}{A_1^*} \ln (1 + x_2 \delta) + \frac{x_2}{A_2^*} \ln (1 - x_1 \delta) \right] \quad (\text{A.12})$$

Since the products  $x_2 \delta$  and  $x_1 \delta$  are much less than unity [2], expansion of the logarithmic terms and retrieving the first term yields

$$\sigma^E = x_1 x_2 RT \left[ \left( \frac{1}{A_1^*} - \frac{1}{A_2^*} \right) \delta \right] \quad (\text{A.13})$$

or

$$\frac{\sigma^E}{x_1 x_2} = RT \left( \frac{1}{A_1^*} - \frac{1}{A_2^*} \right) \delta_p + RT \left( \frac{1}{A_1^*} - \frac{1}{A_2^*} \right) \delta_m x_2^{c'-1} \quad (\text{A.14})$$

Eq. (A.14) can be expressed as Eq. (17) if

$$A = RT \left( \frac{1}{A_1^*} - \frac{1}{A_2^*} \right) \delta_p$$

$$B = \frac{RT}{2C} \left( \frac{1}{A_1^*} - \frac{1}{A_2^*} \right) \delta_m$$

and

$$C = C' - 1.$$

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